Temperature Rising Elution Fractionation of Polypropylenes Produced by Heterogeneous Ziegler–Natta Catalysts Containing Different Internal Donors

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ABSTRACT: Ethyl benzoate (EB), bis(2-ethyl hexyl) sebacate (BEHS), di-*n*-butyl phthalate (DNBP), and bis(2-ethyl hexyl) phthalate (BEHP) were employed as internal electron donors of heterogeneous Ziegler–Natta catalysts and the obtained polypropylene (PP) samples were fractionated by temperature rising elution fractionation (TREF). The influence of different internal donors on the tacticity distributions of PPs was compared. PPs have narrower tacticity distributions with aromatic esters. Based on TREF results, different interactions of internal donor, which may depend on their structures, were proposed. The effects of internal donors on microstructure of the fractions, especially the first fractions, were examined.

KEY WORDS Polypropylene / Ziegler–Natta Catalyst / Internal Donor / Fractionation / Characterization /

Electron donors are key components of Ti-based heterogeneous catalysts for propylene polymerization and have been the subject of many researches.¹ It is well known that MgCl₂-supported Ziegler–Natta catalysts underwent two development stages using aromatic monoester and aromatic diester as internal electron donor, respectively.² Aromatic diester is found to show better performance than aromatic monoester. The differences between aromatic monoester and diester have been studied by many authors.^{3–5} Yang found that diester could interact with TiCl₄, while monoester could not interact with TiCl₄.³ Sacchi discovered that monoester poisoned active sites which produce a prevalently syndiotactic first propylene insertion and/or transformed them into isospecific ones. Diester had not such an effect. Thus, they concluded that diester and monoester interact with the nonstereospecific sites in different ways.⁴ Soga proposed a model to explain the difference of mono- and diester, in which monoester was presumed to be extracted by AlEt₃ more easily than diester.⁵

In this paper, some MgCl₂-supported Ziegler–Natta catalysts employing different ester compounds (including mono- and diesters) as internal electron donors were prepared. The polypropylene (PP) samples obtained from these catalysts were fractionated with temperature rising elution fractionation (TREF) and the influence of different internal donors on the tacticity of PPs was investigated. Based on TREF results, different interactions of these internal donors with active sites were compared.

EXPERIMENTAL

Preparation of the Catalyst

The preparation of MgCl₂-supported catalysts is described in ref 6. Under N₂ atmosphere, 1 gram of anhydrous MgCl₂ and 6 ml BuOH were added to 50 ml *n*-octane. This suspension was heated to 80°C and stirred until MgCl₂ was dissolved. The solution was then heated at 100°C for 2 hours after 50 ml TiCl₄ was introduced. The resulting solid product was separated by filtration

and washed with *n*-octane. Internal electron donors (if needed) was added and stirred for 2 hours. The suspension was washed and 50 ml TiCl₄ was added again. After 2 hours, filtration and washing were repeated.

Polymerization of Propylene

Polymerization was carried out in slurry at atmospheric pressure for 1 hour. Propylene was rapidly bubbled through the stirred *n*-heptane solvent in a reactor. AlEt₃ was used as cocatalyst and diphenyl dimethoxysilane (DPDMS) was employed as external electron donor. Typical polymerization conditions were: 100 ml of *n*-heptane, 30 mg catalysts, [AlEt₃]/[Ti] = 100, [Si]/[Al] = 0.04, polymerization temperature = 50°C. Polymerization reaction was terminated by the addition of ethanol containing HCl. The products were washed and filtrated, then dried *in vacuo* at 80°C overnight.

Preparative TREF

Preparative TREF apparatus was used to collect large fractions of fractionated polymers. 1 gram polymer and 3% antioxidant were added to a 1000 ml flask containing 250 ml xylene. The polymer was dissolved at 130°C. 500 g clean and dry sea sand were heated to the same temperature. The sand was added to the flask and maintained at 130°C for 2 h. The mixture was cooled to room temperature at a rate of 1.5°C h⁻¹. The cooled sand wrapped with polymer was transferred into a steel column with a temperature controlling unit. The sand was heated in increment of temperature and eluted with xylene. The polymer was recovered by evaporating the xylene solvent and drying in a vacuum oven. Because a small amount of antioxidant is added, the recovery of polymer is 105% or so.

NMR Analyses

¹³C NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 100.7 MHz in PFT mode at 370 K. The polymer solutions were prepared by dissolving *ca.* 50 mg polymer in 0.5 ml C₆D₄Cl₂. 1% hexamethyldisiloxane (HMDS) was added as the internal ref-

Table I. Ti content, activity of different catalyst and some characteristics of whole samples

Internal donor	No	EB	BEHS	BEHP	DNBP
Ti content/wt%	4.58	3.63	3.18	3.31	2.57
Activity	7.82	4.38	1.57	4.01	4.74
(KgPP/gTi hour)	5.62	1.91	0.77	3.24	4.19
$m\%$ (whole) ^{b,c}	87.6	96.5	96.0	98.0	98.0
$\bar{M}_w (\times 10^{-4})$	25.11	30.82	27.63	32.45	31.53
$\bar{M}_w/\bar{M}_n$	11.82	10.54	10.67	10.07	10.35

^a External donor was not added. ^b External donor used. ^c Determined by ¹³C NMR.

Figure 1. TREF curves of PP prepared by different catalysts: (a) $\text{TiCl}_4/\text{MgCl}_2/\text{EB-Al}(\text{C}_2\text{H}_5)_3/\text{DPDMS}$, (b) $\text{TiCl}_4/\text{MgCl}_2/\text{DNBP-Al}(\text{C}_2\text{H}_5)_3/\text{DPDMS}$.

erence. The pulse angle was 90° , pulse repetition 10 s, spectral width 5000 Hz, number of scans was 6000, and data points 32 K.

RESULTS AND DISCUSSION

Ethyl benzoate (EB, A), bis(2-ethyl hexyl) sebacate (BEHS, B), di-*n*-butyl phthalate (DNBP, C), and bis-(2-ethyl hexyl) phthalate (BEHP, D) were used as internal donors and four catalysts containing different internal donors were prepared. Polymerization activity of different catalysts and some characteristics of the whole polymers such as molecular weight, molecular weight distribution, and isotacticity are listed in Table I. All internal donors decrease catalytic activity, but a relatively high activity is retained for the catalysts containing aromatic diester as internal donor (C and D). There is considerable increase in isotacticity after ad-

Table II. TREF data of sample A

No.	$T/^\circ\text{C}$	$W_i \%$	$\sum W_i \%$	$W_i \%/ \Delta T$
1	18	8.129	8.29	—
2	40	1.892	10.021	0.0860
3	60	3.224	13.245	0.1612
4	70	4.975	18.220	0.4975
5	80	3.854	22.074	0.3854
6	85	3.644	25.718	0.7288
7	91	4.765	30.493	0.7942
8	96	6.027	36.510	1.2054
9	100	3.574	40.084	0.8935
10	103	5.466	45.550	1.8220
11	106	9.460	55.010	3.1533
12	109	8.409	63.419	2.8030
13	112	22.14	85.563	7.3810
14	115	11.49	97.056	3.8310
15	118	1.542	98.598	0.5140
16	122	1.261	99.859	0.3153
17	129	0.140	99.999	0.0200

Table III. TREF data of sample B

No.	$T/^\circ\text{C}$	$W_i \%$	$\sum W_i \%$	$W_i \%/ \Delta T$
1	18	10.818	10.818	—
2	39	4.415	14.963	0.2102
3	61	1.736	16.699	0.0789
4	70	1.407	18.106	0.1563
5	81	4.175	22.281	0.3795
6	85	2.065	24.346	0.5163
7	90	2.245	26.591	0.4490
8	95	2.394	28.985	0.4788
9	100	4.938	33.923	0.9876
10	103	4.130	38.053	1.3767
11	106	4.684	42.737	1.5613
12	109	14.54	57.281	4.8480
13	112	1.392	58.673	0.4640
14	115	8.245	6.918	2.7483
15	119	17.48	84.395	4.3693
16	124	4.100	88.495	0.8200
17	130	11.51	100.002	1.9178

dition of internal donor in the catalyst, and the polymers produced by catalyst C and D possess the highest isotacticity. Internal donors increase the molecular weight and narrow the molecular weight distribution of whole polymer.

TREF results of PPs prepared with catalysts containing B and D as internal electron donor have been reported previously.⁷ Here, two additional PP samples were presented (Figure 1), prepared with catalysts using A and C as internal electron donors, respectively. The fractionation data of these four samples (A—D) are summarized in Tables II—V. The GPC curves of some selected fractions of sample D are shown in Figure 2. One can see that the molecular weight of fractions

Table IV. TREF data of sample C

No.	$T/^{\circ}\text{C}$	W_i %	ΣW_i %	W_i %/ ΔT
1	15	8.525	8.525	—
2	40	1.364	9.889	0.0546
3	60	1.449	11.338	0.0725
4	70	1.449	12.787	0.1449
5	80	1.876	14.663	0.1876
6	85	2.387	17.050	0.4474
7	90	0.256	17.306	0.0512
8	93	1.279	18.585	0.4263
9	96	1.620	20.205	0.5400
10	99	2.643	22.848	0.8810
11	102	4.177	27.025	1.392
12	105	5.541	32.566	1.847
13	108.5	11.253	43.819	3.294
14	112	38.704	82.523	11.058
15	115	10.827	93.350	3.609
16	120	4.689	98.039	0.938
17	127	1.961	100.00	0.230

Table V. TREF data of sample D

No.	$T/^{\circ}\text{C}$	W_i %	ΣW_i %	W_i %/ ΔT
1	12	8.655	8.655	—
2	42	1.867	10.522	0.06237
3	60	3.012	13.534	0.1672
4	71	3.140	16.674	0.2855
5	80	3.564	20.238	0.3958
6	85	2.843	23.081	0.5685
7	89	2.843	25.924	0.7106
8	95	2.970	28.894	0.4951
9	100	3.222	32.118	0.6449
10	103	5.218	37.336	1.7395
11	106	5.600	42.936	1.8668
12	109	7.000	49.936	2.3335
13	111	8.358	58.294	4.1578
14	115	30.42	88.714	7.6071
15	118	8.485	97.199	2.8300
16	121	1.612	98.811	0.5388
17	124.5	0.679	99.490	0.1952
18	130	0.509	99.999	0.0925

Figure 2. GPC curves of selected fractions of sample D.

increases with elution temperature, but all fractions have a broad molecular weight distribution. Consequently, molecular weight is not the most important factor in the fractionation and TREF method fractionates polymer mainly based on tacticity.^{8,9} The increase of molecular weight with elution temperature may be due to the coincidence of molecular weight and tacticity.

From the shapes of these TREF curves, one can see

Table VI. Comparison of fractionation data for different PP sample

Sample ^a	A	B	C	D	E ^b	F ^c	G ^d
W_i %	8.13	10.82	8.52	8.65	9.45	15.27	9.74
ΣW_i % (<100°C)	40.01	33.92	22.85	32.12	42.91	59.27	39.80
Maximal W_i %/ ΔT near 103°C	3.15	4.85	1.39	1.74	1.42	1.87	1.98
Maximal W_i %/ ΔT near 115°C	7.38	4.37	11.05	7.61	5.07	3.45	5.64

^a Internal electron donors for the samples are EB(A), BEHS(B), BEHP(C), and DNBP(D), respectively. ^b Only external donor DPDMS was used. ^c Neither internal donor nor external donor was used. ^d Only internal donor DNBP was used.

that internal donors have great influence on the tacticity of PPs. Above 100°C only single large peak was observed in the W_i %/ ΔT - T curve when BEHP was used as internal electron donor, while two peaks appeared near 103°C and 115°C in the case of BEHS. A detailed comparison of TREF data for these samples is summarized in Table VI. All internal donors do not decrease the amount of atactic fraction (first fraction) largely when external donor is added in the polymerization. However, this effect is more evident in the absence of external donor (sample F and G). A reasonable explanation is that the external donor can take larger effect when catalyst contains no internal donor. Sacchi *et al.* suggests that external donor could partly replace internal donor as internal donor was removed by AlEt_3 .¹ A similar case is the whole amount of fractions eluted below 100°C, which are of low isotacticity (see Table VII). The internal donor can decrease the proportion of this part.

W_i %/ ΔT at 115°C is much larger than that at 103°C when aromatic diesters (BEHP and DNBP) were used as internal electron donors. In contrast, W_i %/ ΔT near 115°C and 103°C are almost the same in the case of BEHS. These two values are moderate for the aromatic monoester EB. In conclusion, PPs produced by the catalysts containing aromatic diester as the internal donor have narrower tacticity distribution. The fractions eluted at room temperature, 80°C, 103°C, and 115°C were selected for ¹³C NMR analysis and the pentad distributions are listed in Table VII. As shown in Table VII, the isotacticity of the fractions eluted at room temperature and 80°C is low, while the isotacticity of the fractions eluted above 100°C is considerably high. The difference in tacticity of these four fractions indicates they are produced by different active sites. The fractions eluted below 100°C may be generated by active sites with low stereospecificity and those eluted above 100°C may result from isospecific active sites. The existence of more than one isospecific active site agrees with the results of Kakugo.¹⁰

Since internal electron donors influence the tacticity distributions of PPs, one may conclude that internal electron donors can convert aspecific active sites into two isospecific active sites and internal electron donors are present in the environment of isospecific active sites. However, the conversion of aspecific active sites into isospecific ones varies with the internal electron donor.⁷ Based on the results of TREF, the following model of interaction between internal electron donors and active sites is proposed (Scheme 1).

Table VII. Observed pentad distributions of some fractions^a

Elution temp	Fraction ^b	<i>mmmm</i>	<i>mmmr</i>	<i>rmmr</i>	<i>mmrr</i>	<i>mrmm</i> + <i>rrmr</i>	<i>mrmr</i>	<i>rrrr</i>	<i>rrrm</i>	<i>mrrrm</i>	Inverted units/%
r.t. ^c	1/A	26.8	12.9	3.2	15.4	11.2	2.3	12.6	7.7	7.9	—
	1/B	29.5	11.4	2.5	14.9	9.6	1.0	15.6	9.3	6.2	—
	1/C	19.6	9.0	3.3	15.5	16.1	3.0	12.6	9.8	8.1	3.6
	1/D	22.9	12.5	2.7	16.3	14.1	2.7	10.3	9.9	8.6	—
80°C	5/A	71.1	7.8	0	8.9	1.2	0	2.8	2.3	6.0	—
	5/B	70.0	3.1	6.3	7.1	0	0	2.7	3.1	7.8	—
	5/C ^d	—	—	—	—	—	—	—	—	—	—
	5/D	73.6	7.1	0.9	7.2	1.8	1.4	2.0	2.4	3.4	—
103°C	10/A	87.6	4.9	0	4.2	0	0	1.1	0	2.2	—
	12/B	88.7	4.3	0	4.8	0	0	0	0	2.2	—
	10/C	92.0	2.5	0	3.5	1.8	0	0	0	2.2	—
	10/D	91.9	2.7	0	2.8	1.0	0	0.6	0	1.0	—

^a *mmmm* content for all fractions eluted near 115°C is 100% and not listed. ^b Internal electron donors for the samples are EB(A), BEHS(B), BEHP(C), and DNBP(D). ^c Room temperature. ^d This fraction was not tested because of the too small amount.

Scheme 1. Interactions of internal electron donors with aspecific active sites on the (100) face.

It is widely accepted that mononuclear Ti atom supported on the (100) face of MgCl_2 is a source of aspecific active sites.^{11,12} The coordinate number of mononuclear Ti^{4+} ions on the (100) face of MgCl_2 is 5 and the coordinatively unsaturated number (vacant site) is 1. Since internal electron donors contact the active sites before Ti^{4+} ion is reduced to Ti^{3+} ion by AlEt_3 , only one functional group of internal electron donor can

be used to coordinate with Ti^{4+} ions. After Ti^{4+} ion is reduced to Ti^{3+} ion by cocatalyst, a new vacant site is generated, while the coordination of the internal electron donor with active sites is unaffected. In the case of the aromatic diester, two carbonyls cannot associate with active sites simultaneously. Nevertheless, since the aspecific active site is mononuclear, the Mg atom of the support adjacent to the active site is uncovered. One carbonyl of aromatic diesters may coordinate with this Mg atom (Site-1). Site-1 is similar to that proposed by Soga.⁵ The simultaneous coordination of aromatic diester with Ti and Mg atom forms a bridged structure, which leads to high rigidity of active sites. Such a structure also makes it not easy to be removed by AlEt_3 . The active sites may produce the most highly isotactic fractions eluted near 115°C. When aromatic monoester is used as the internal electron donor, the only one carbonyl associates with the aspecific active sites on (100) face of MgCl_2 . There are two cases for the Mg atom adjacent to the active sites: coordinating with another monoester molecule (Site-2a) or not (Site-2b). Site-2a is highly steric and less flexible, which may also produce the most highly isotactic fractions. Compared with Site-2a, Site-2b is less steric and more flexible, and it may produce less isotactic fractions eluted around 103°C. Due to coexistence of two carbonyls in the same molecule and suitable length between them, the association of the aromatic diester with aspecific active sites on (100) face results in Site-1 mostly, while Site-2a may not be produced so readily, since the formation of Site-2a needs the cooperation of two different molecules. Therefore, sample C contains more fractions eluted near 103°C than sample A. In the case of BEHS, one carbonyl can interact with aspecific sites. However, long distance between the two carbonyl makes it impossible for the other carbonyl in the same molecule to coordinate with the Mg atom adjacent the active sites. The presence of long aliphatic alkyl prevents association of another BEHS molecule with this Mg atom. The overall results lead to complete conversion of aspecific active sites to less isospecific ones, which produces the less isotactic fractions eluted near 103°C, instead of the most highly isospecific ones.

There is a common characteristic of pentad distributions of the first fractions in Table VII. The amount of

Table VIII. Estimation of average length of continuous *m* and *r* sequences and MW and MWD of the first fractions

Internal donor	EB	BEHS	BEHP	DNBP	DNBP ^a
<i>l(m)</i>	7.15	8.18	7.35	6.66	11.32
<i>l(r)</i>	6.27	6.35	5.57	5.18	7.28
<i>l(m)*l(r)</i>	44.8	51.9	40.9	34.4	82.40
$\bar{M}_w (\times 10^{-4})$	3.62	3.45	2.93	3.14	4.34
$\bar{M}_w/\bar{M}_n$	4.53	4.42	4.01	4.12	5.27

^a External donor not added during polymerization.

[*mmmm*] is larger than that of [*mmmr*] and the amount of [*rrrr*] is larger than that of [*rrrm*], which means that the same configuration as the last configuration of the propagating chain is formed continuously. This may result in stereoblock structures to some extent. The average length of continuous *m* and *r* sequences can be estimated from pentad distributions and it is influenced by both internal and external donor.^{13,14} The values for the polymers produced by different catalysts are listed in Table VIII. The large *l(m)*l(r)* for all samples suggest that stereoblock structures are formed. Stereoblock structures were earlier found in the atactic fractions prepared with supported Ti-based catalysts by Busico.¹⁵ On comparing different internal donors, *l(m)*l(r)* are smaller for BEHP and DNBP than that for BEHS and EB. This indicates that monoesters lead to large stereoblocks, which may be related to the easier removal of monoesters by AlEt₃. When external donor is not added during the polymerization, the obtained polymer fraction has the largest *l(m)*l(r)*, suggesting that internal donor is more readily removed by AlEt₃ in the absence of external donor and external donor can reduce the ability of AlEt₃ to remove internal donor.¹

The molecular weight and molecular weight distribution of the first fractions are listed in Table VIII. All internal donors decrease the molecular weight and narrow the molecular weight distribution of this fraction to different extents, and aromatic diesters are more effective. This suggests that the internal donor selectively interacts with active sites which produce relatively higher molecular weight in aspecific active sites. In our other work, we found that the isotacticity of the first fraction decreased when the internal donor was introduced in the

catalyst.¹⁶ Thus, we can conclude that the aspecific active sites interacting with internal donor are relatively more stereospecific.

Examining the isotacticity of first fractions in Table VII, one can see that fraction 1/A and 1/B have higher isotacticity than fractions 1/C and 1/D have, though samples A and B have lower whole isotacticity. This shows that BEHP and DNBP have better performance than EB and BEHS and this is not due to increased isotacticity of the fractions, but due to increased amounts of high isotactic fractions.

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